Important considerations in applying X-ray Microanalysis techniques for the diagnosis of outdoor copper based monuments

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A Diagnosis Process for Damage Assessment of Monuments

- Documentation, visual examination, historical/archival research, photographic records
- Surveying surroundings, decay mapping etc
- Design of plans for sampling and measuring
- Non-invasive analysis in-*situ*
- Sampling (direct or indirect)
- and analysis
- (nondestructive and destructive)
- CEN/TC 346 WG2 draft standard

Diagnosis of Surface and Structure

Purpose of Presentation

- how diagnostic analysis using XRF and XRD can best be applied for the outdoor copper based monuments
- best systematic approach to apply such techniques for a complete damage assessment of the monument
- highlights the benefits of non-invasive in-situ analysis, but also the limitations
- important information that can and should be obtained in many instances through destructive analysis.
- Case studies: Theseus in Athens, and Kolokotronis monuments in Athens and Nauplion

Kolokotronis in Nafplion and Athens

Brief History of Kolokotronis

- Nauplion cast in 1896 at the foundry of Thiebaut brothers in Paris
- sculptor Lazaros Sochos
- Nauplion erected in 1900
- only 100 m from the seaside.
- Athens erected in 1904 in one of the busiest and polluted streets in the city.

SO2 and RH

- ***Figure 1.*** *Mean Annual SO_2 concentrations in Athens and Nafplion*

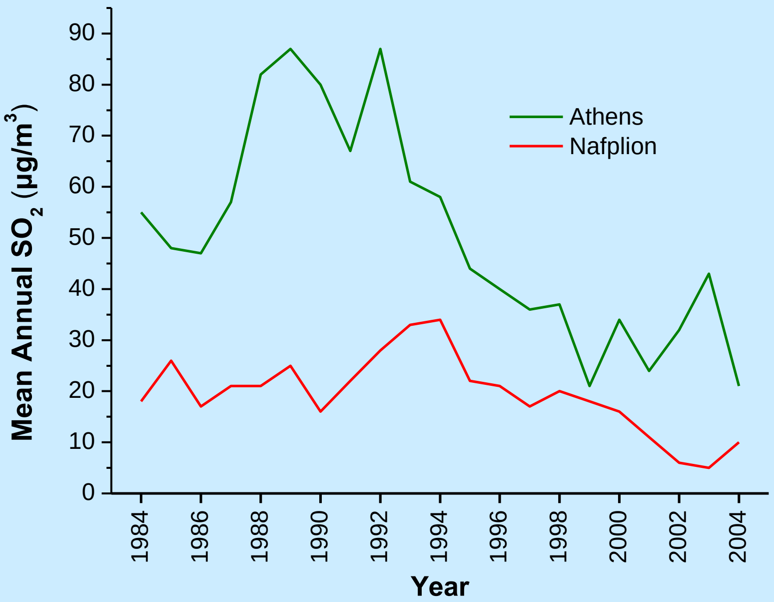
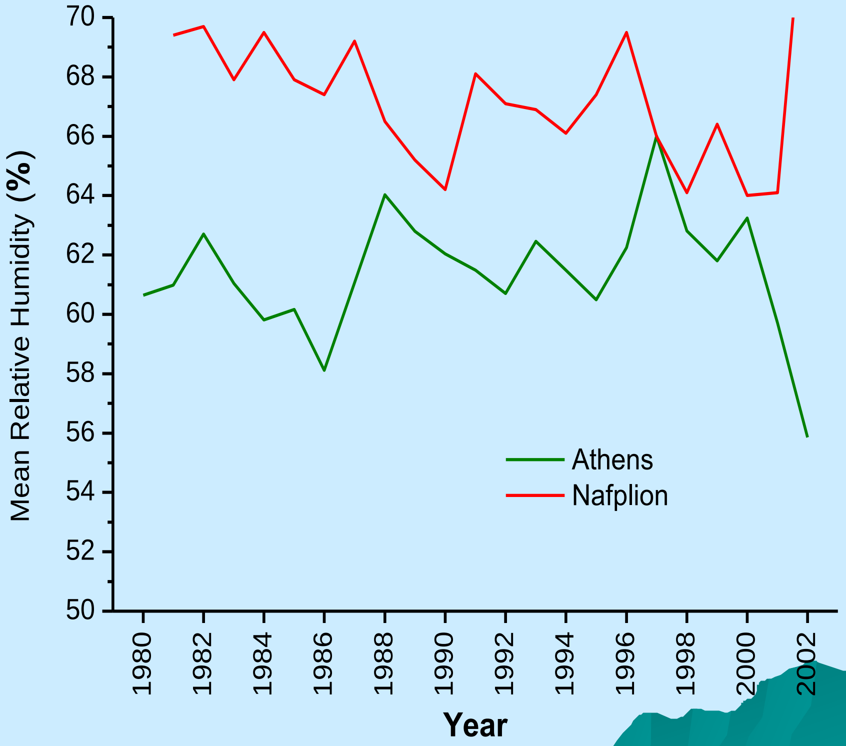
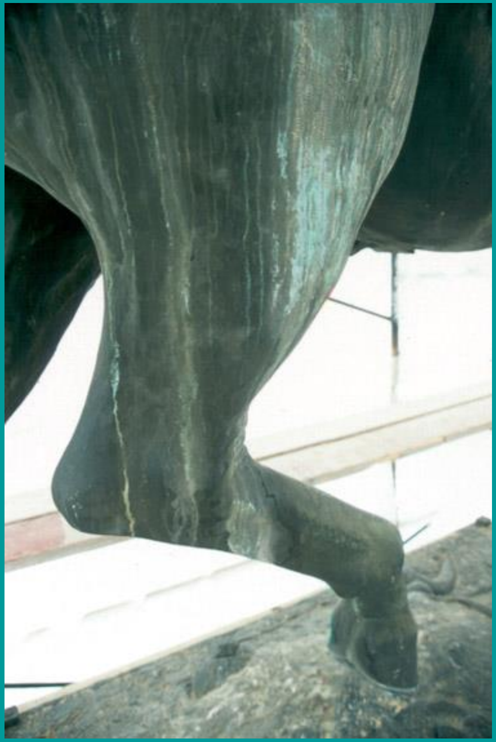


Figure 2. *Mean Relative Humidity for Athens and Nafplion*



ATHENS

BLACK PATINA



STREAKING

GREEN PATCHES

BLACK CRUST

Black Patina

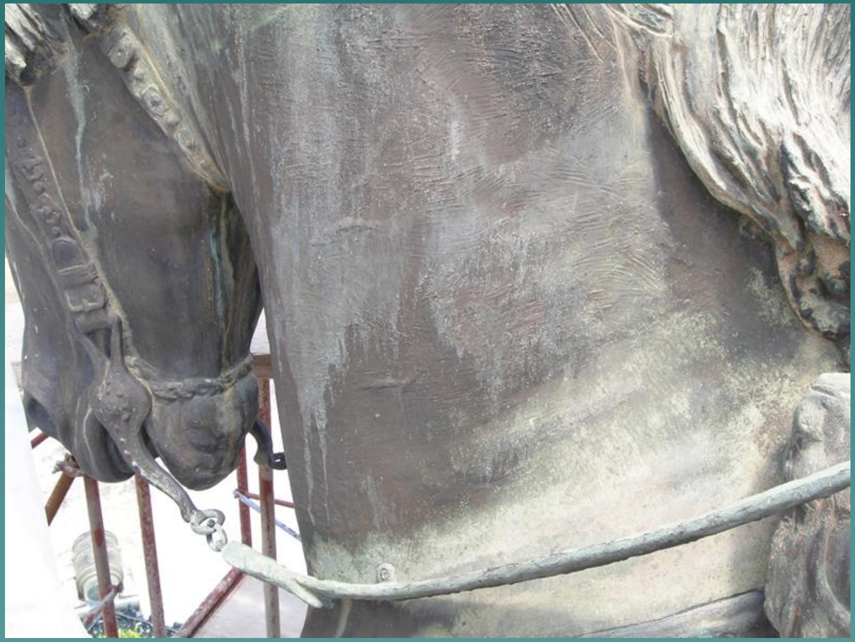
Chased Surface of Horse

Athens Nafplion

Athens

Nafplion

Nafplion – Pitting Corrosion



Selection of Sampling or Location of Measurements

- Monument's construction technique (materials, structure, morphology)
- Surface characterization (surface inclination, surface texture, orientation, colour, texture, coverage, adhesion, crust types, patina, presence of fillers, coatings or other materials) (surface area in terms of orientation)
- Cracks and other types of physical damages
- preliminary assessment of environmental/climatic and microclimatic data in relation to monument
  (rain/sun sheltered, exposed to wind/water/sun, in direct contact with wind/water, rain/water flow etc),

Sampling Plan

XRF Analysis by Team from Demokritos

Portable XRF in 2001

- The instrumentation included two point radioactive sources, a Cd-109 and an Am-241, a peltier cooled PIN x-ray detector working at room temperature exhibiting a resolution of 240 eV at 5.9 keV, (XR-100T, Amptek Inc) and a battery operated aquisition card (MCA8000A, Amptek Inc.).
- radioactive sources are convenient and simple for bulk alloy analysis due to their monochromaticity
- Huge disadvantage**:** They are radioactive materials and handling as well as transportation is not an easy task.

XRF Results in %w/w on precleaned areas of Athens statue

A/A	Position	Cu	Zn	Sn	Pb
1	Kolokotronis, left stir-up, heel	89.5	5.0	5.5	<0.7
2	Horse, right front leg	90.0	4.9	5.1	<0.7
3	Kolokotronis, helmet next to epigraphy	90.4	3.4	6.2	<0.7
4	Kolokotronis, upper body	91.2	3.2	5.6	<0.7

A/A	Position	Zn/Cu (% w/w)	Sn/Cu (% w/w)	Other Metals	Treatment	Description
1	Kolokotronis, helmet, next to the epigraphy	4.4	-	Fe, Pb	no	patina surface
2	-“-	2.4	8.2	-	yes	patina surface
3	-“-	3.8	6.9	-	-	clean surface
4	Kolokotronis, upper body	2.3	7.7	-	yes	patina surface
5	-“-	3.5	6.1	-	-	clean surface
6	Kolokotronis, left stir-up, heel	5.6	6.1	-	-	Clean surface
7	Horse, right front leg	5.4	5.7	-	-	Clean surface
8	Kolokotronis, face, left cheek just under eye	2.9		Fe, Pb	no	Patina surface
9	Kolokotronis, left screw on the belt	5.6		Fe	no	brazing area
10	Kolokotronis, left hand, second joint	4.9		Fe, Pb	no	corrosion green products
11	Kolokotronis, screw on the strap of the left side of breast	6.7		Fe, Pb	no	Patina surface
12	Kolokotronis, back side of left strap above the screw	4.7		Fe, Pb	no	Patina surface
13	Kolokotronis, back side left strap with screw	4.1		Fe, Pb	no	Patina surface
14	Kolokotronis, left hand, up knuckle of the forefinger	3.7		Fe, Pb	no	Patina surface
15	Kolokotronis, Skirt, right side	4.2		Pb	no	corrosion layer with scraches revealing metal
16	bridle	3.5		Pb	no	red corrosion layer

Pilot study of portable XRF system in Nauplion

Portable XRF in 2006

- The spectrometer consists of a low power (3W), cool cathode, transmission anode (Ag) X-ray tube, and Si-PIN detector.
- Unfortunately the specific tube high voltage setting cannot exceed 30 kV
- Sn has to be analyzed using its L characteristic X-ray lines excited by the low energy continuum without the use of any filter
- Tube cooling issues become then of great importance

Nauplion –XRF results

Element	Concentration (%)
Fe	0.32 ± 0.02
Cu	90.9 ± 0.2
Zn	4.7 ± 0.1
As	0.15 ± 0.03
Pb	0.27 ± 0.02
Sn	3.6 ± 0.1

XRD in 2001 and 2006

- Siemens D500, X-Ray Diffraction system
- less then 20mg and zero Background (Si) sample holders were used to minimize the background
- DIFFRACPlus software (Brucker AXS) and JCPDS Powder Diffraction File
- In 2006, quantitative phase analysis was carried out using the Rietveld Method (TOPAS software, Brucker)
- relative percentages of the crystalline phases normalized to sum to 100%.

XRD Analysis in 2001

Black crusts made up of gypsum, and/or calcite and quartz.

Other corrosion products found were

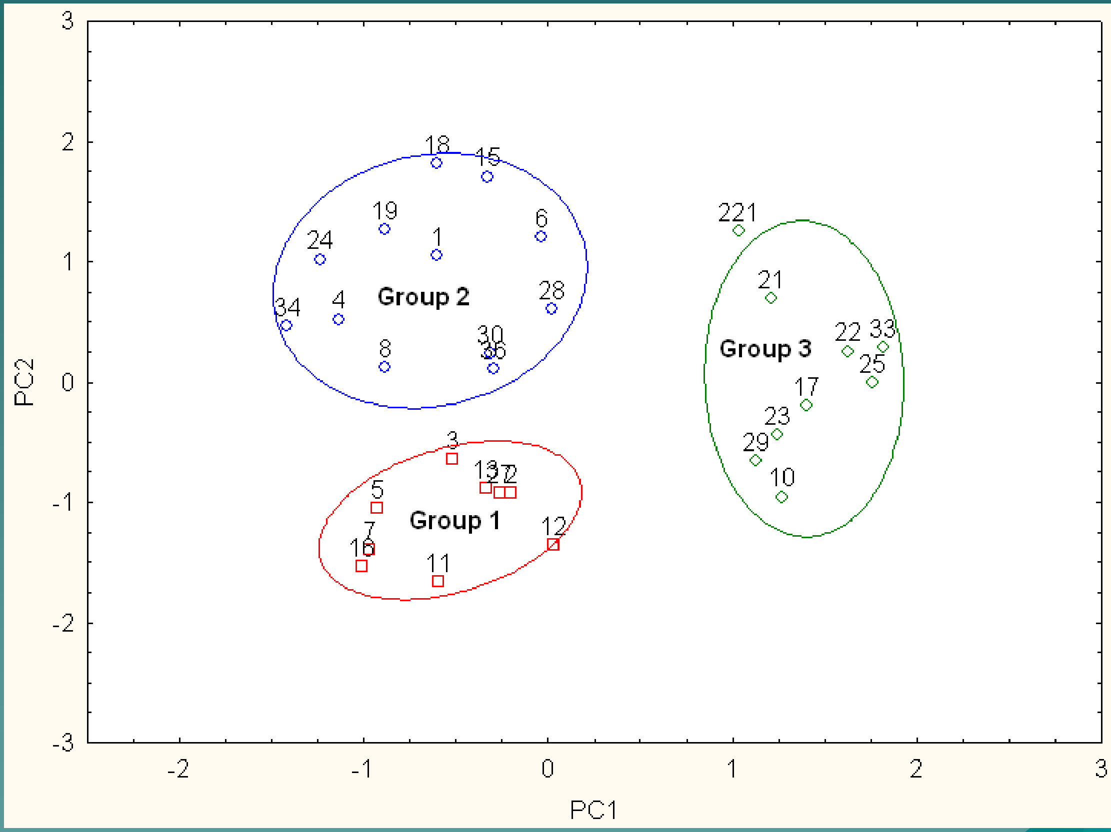
-Bronchantite $CuSO_4 3Cu(OH)_2$

-Atacamite $Cu_2(OH)_3Cl$

-tin oxide SnO_2

Nauplion

- Group 1:Black Crusts Sheltered
- Group 2: Atacamite, Antlerite, Quartz, RainProtection
- Group 3: Brochantite, Calcite, RainWater, Wind

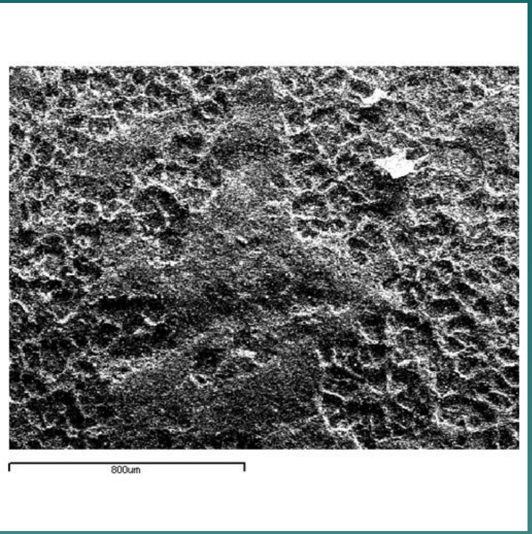


XRD in 2006

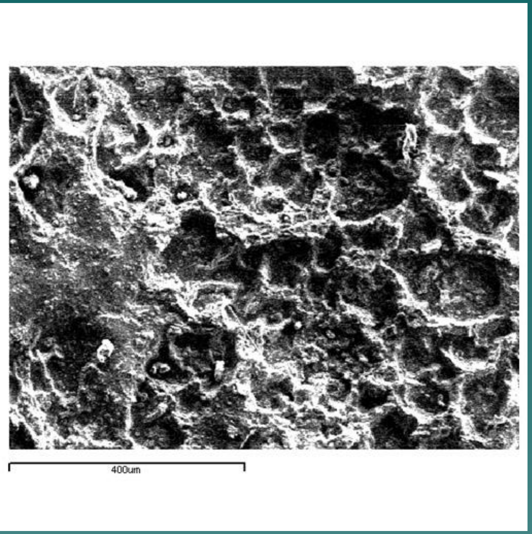
- Quantitative Analysis was carried out
- quantity of corrosion products is larger in Nafplion than in Athens due to conditions
- larger the quantity of crystalline phases in the sample, the better statistics we have when we measure the counts for each phase, so the quantitave analysis is easier.
- crystallisation of corrosion products is better at Nafplion than Athens due to the conditions
- Athens, the sample more amorphous or at least less well crystallised phases, which do not result in well shaped peaks
- this creates problems to the fitting process and consequently to the quantification potential of the software

Making of Molds for documentation of Surface texture in 2001

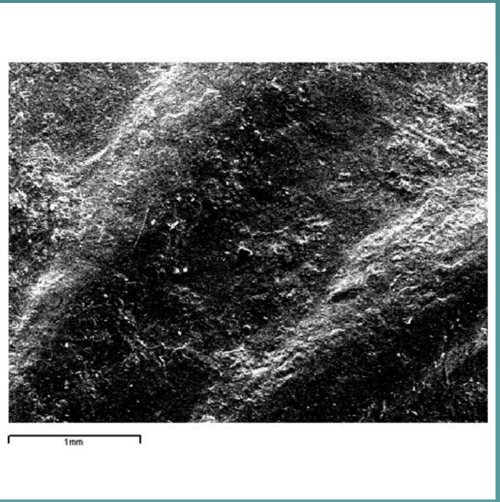
Chased Surface at magnification of x35 and x150



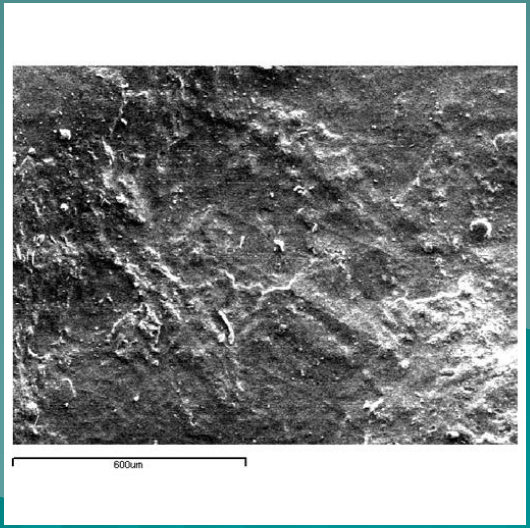
Leg of Horse



Smooth Surface at magnification of x35 and x 100



Sleeve of Kolokotronis



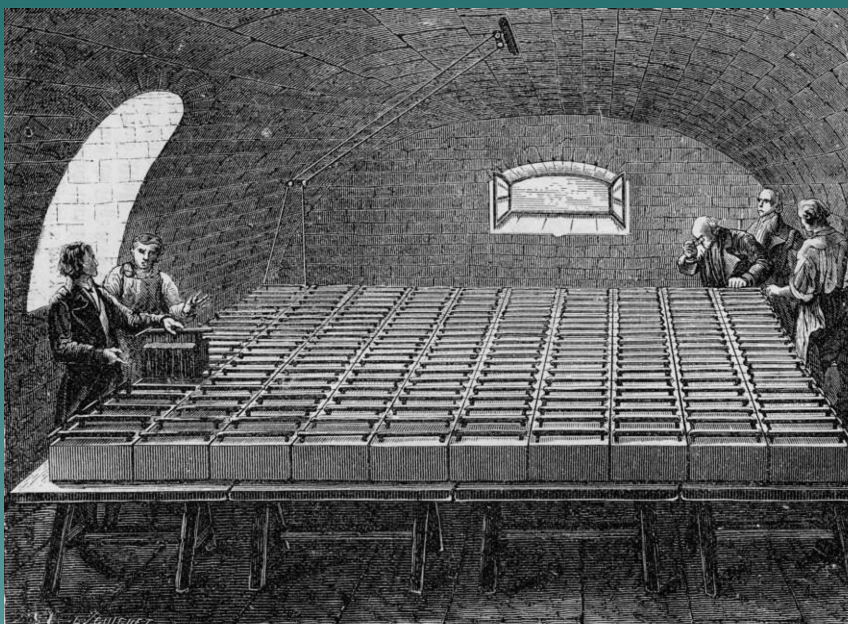
Theseus

by Johannes Pfuhl in 1907

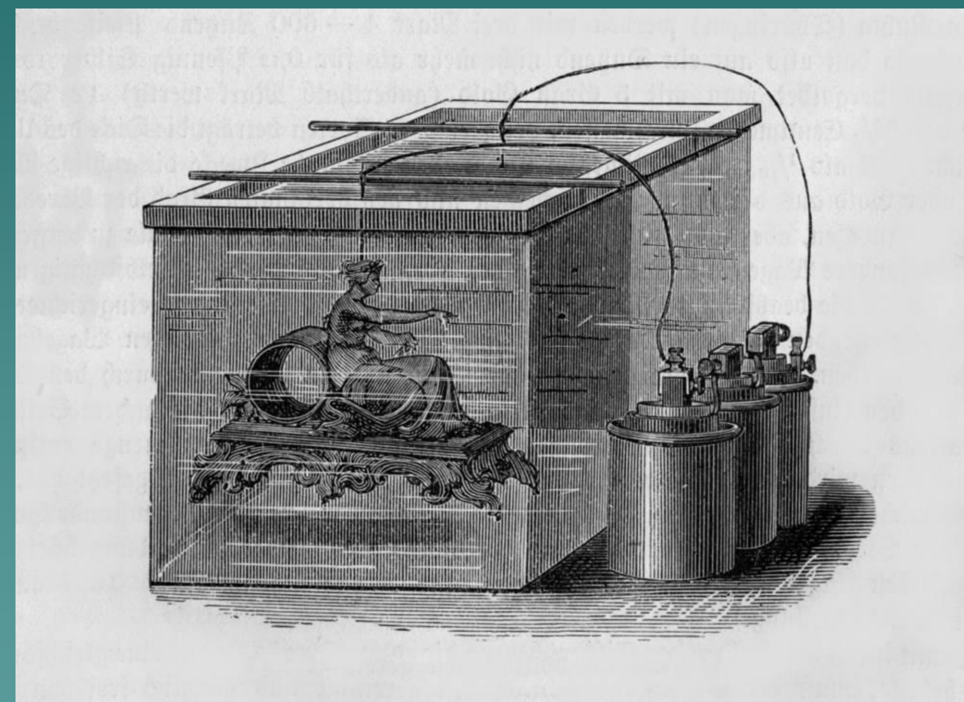
- Looks and sounds like cast bronze but copper
- ‘Hollow type’ expensive to make as opposed to ‘Core type’
- Key is thickness of wall
- Good replication technique

Electrotype technology

German WMF company founded an electrotype department in 1890



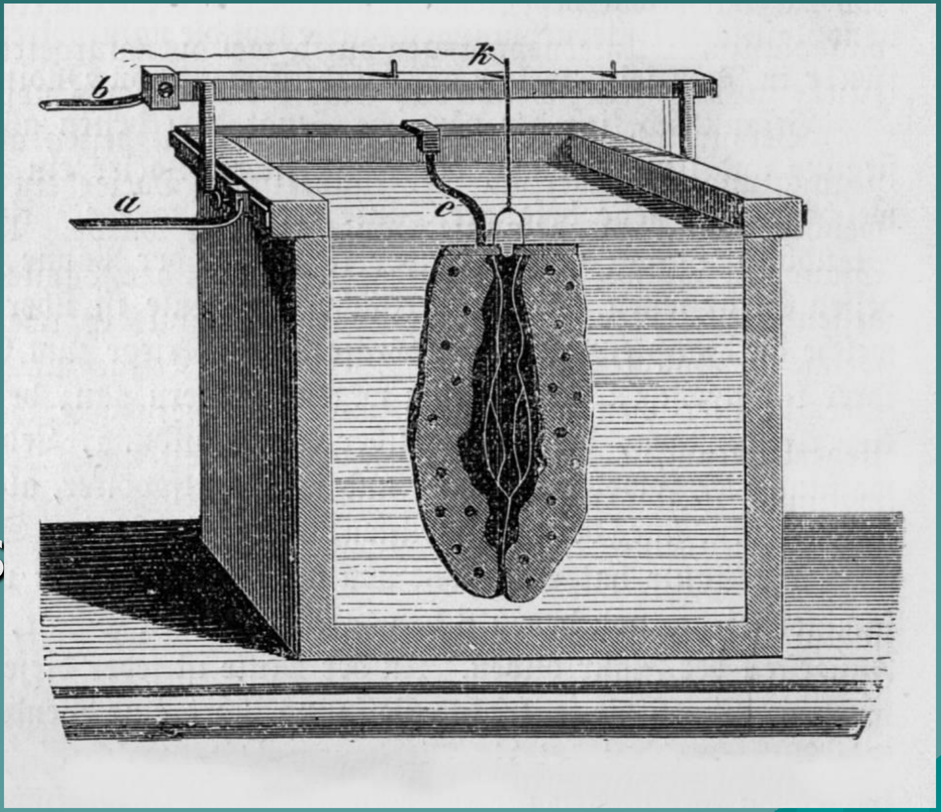
Voltaic power source in the laboratory of the chemist Sir Humphry Davy (1778-1829) made up of 200 copper-zinc galvanic elements



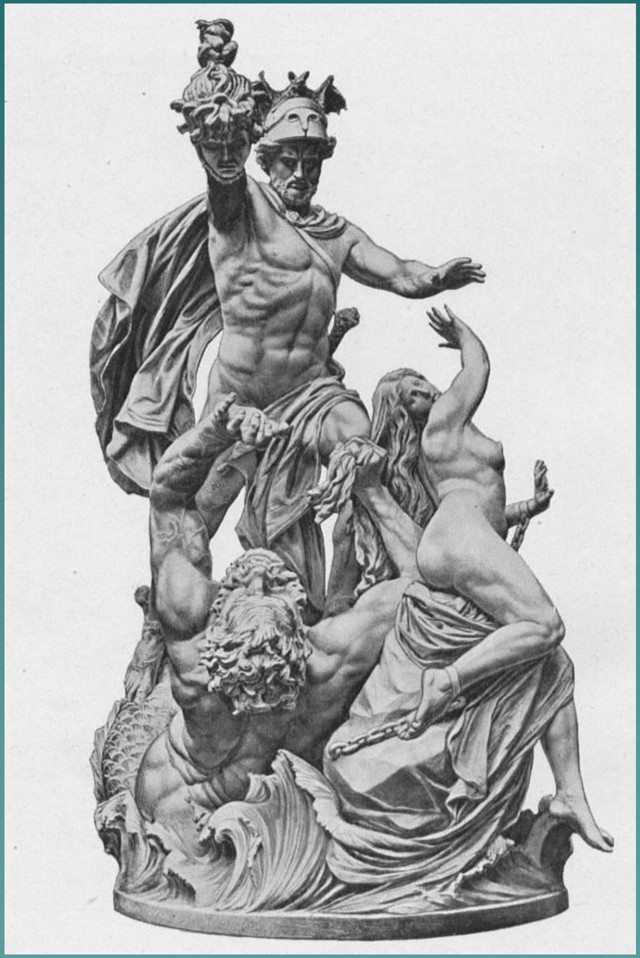
Schematic diagram of the “core type” process.

“Hollow Type” Process

- Graphite layer on mold (negative)
- Thin wire net in galvanic liquid (positive)
- Thicker walls than ‘Core type’ process
- No gypsum is required for core



Famous monuments in Poland and Germany

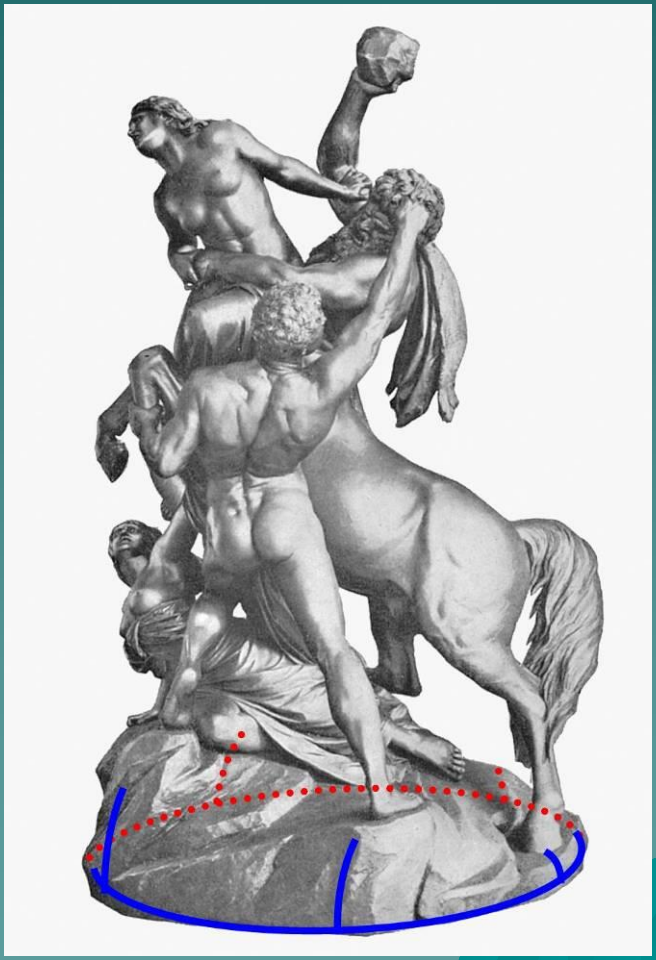


cracks - disequilibrating actions within the sculpture. the plinth is not able to absorb the complete weight of the overlying parts of the monument.


Fenix L2D

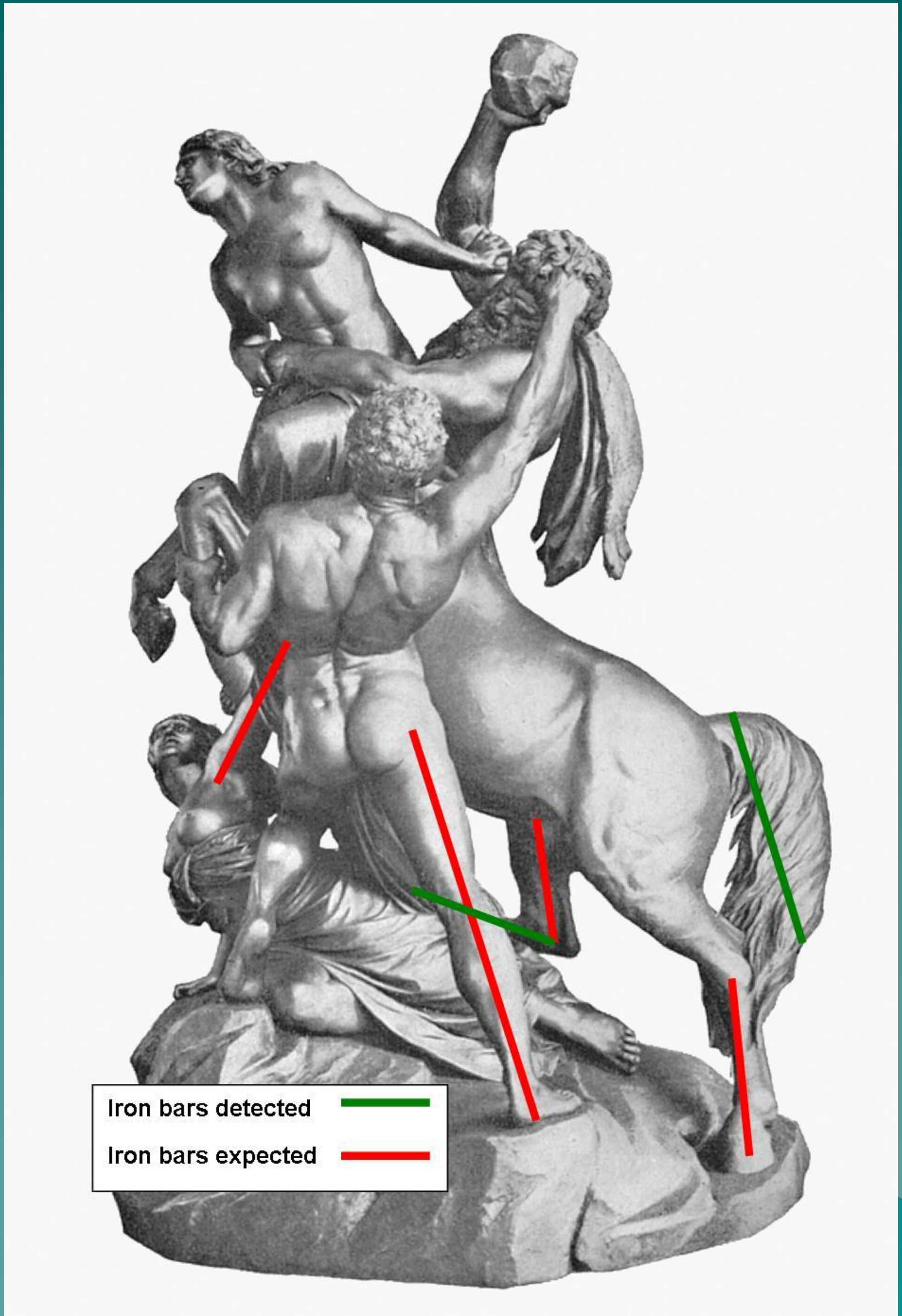
Visual Examination with an endoscopic and a digital camera

- The plinth inside is stabilised by an afloat base-ring build up of pig iron
- On this base-ring there are 5 tubes mounted vertically to stabilise the upper parts of the plinth



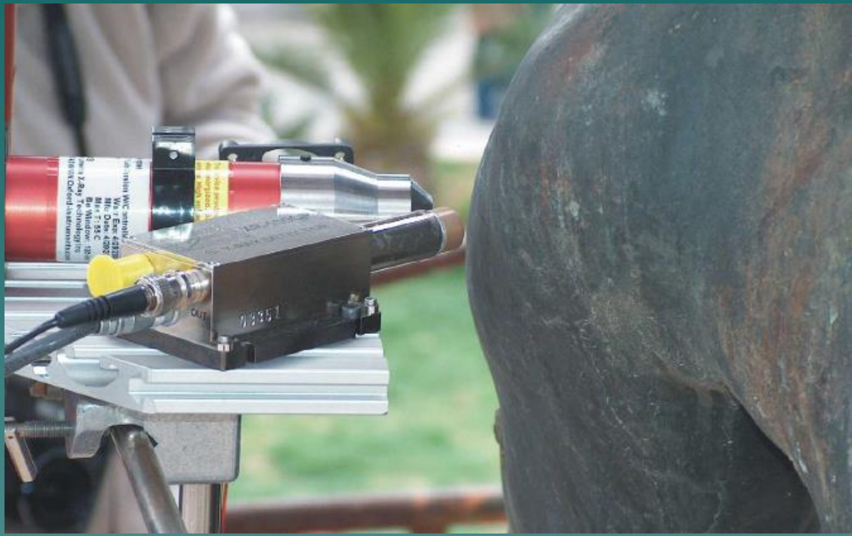
The iron base-ring is heavily corroded partially consisting of layered rust and partially already vanished.

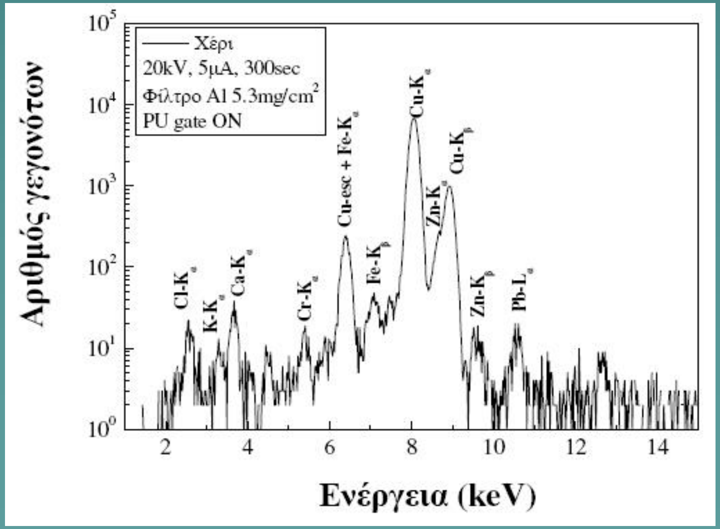
- The iron stilts, which were covered by a galvanic coating, are corroded, too.
- the stilts lost the ability to bear the weight of the sculpture. As a consequence
- the stilts caved in and the galvanic coating burst off as it is shown on the images.

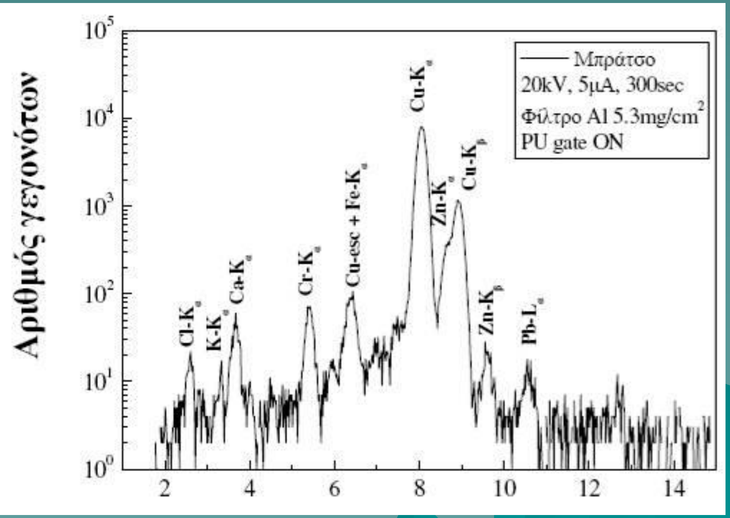

Iron bars detected
Iron bars expected

- This burst fissure is a clear indication for a transversal and lateral shift of the upper part of the monument.
- If this process will proceed, it can be expected that the complete sculpture will lose its integrity and will break down some day.

Portable XRF right hand of lying lady

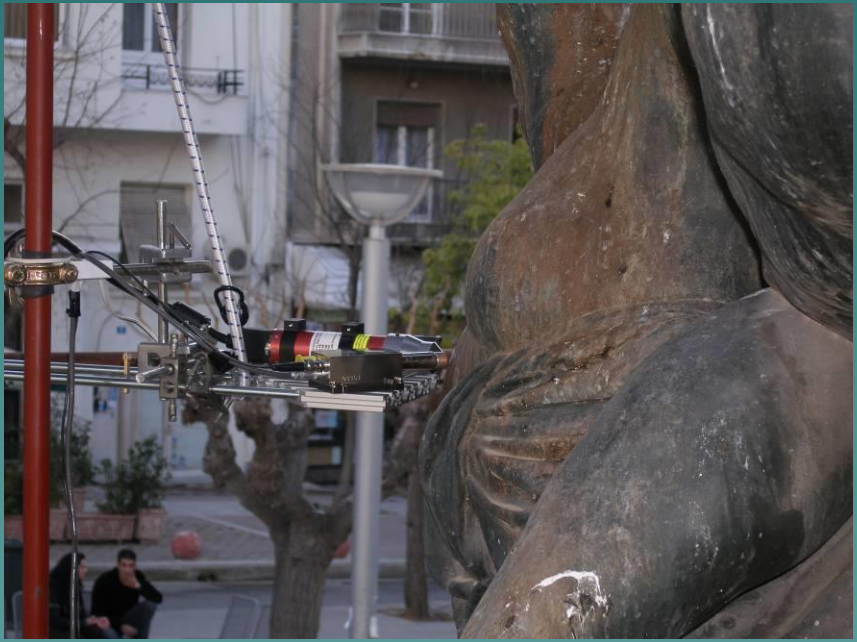


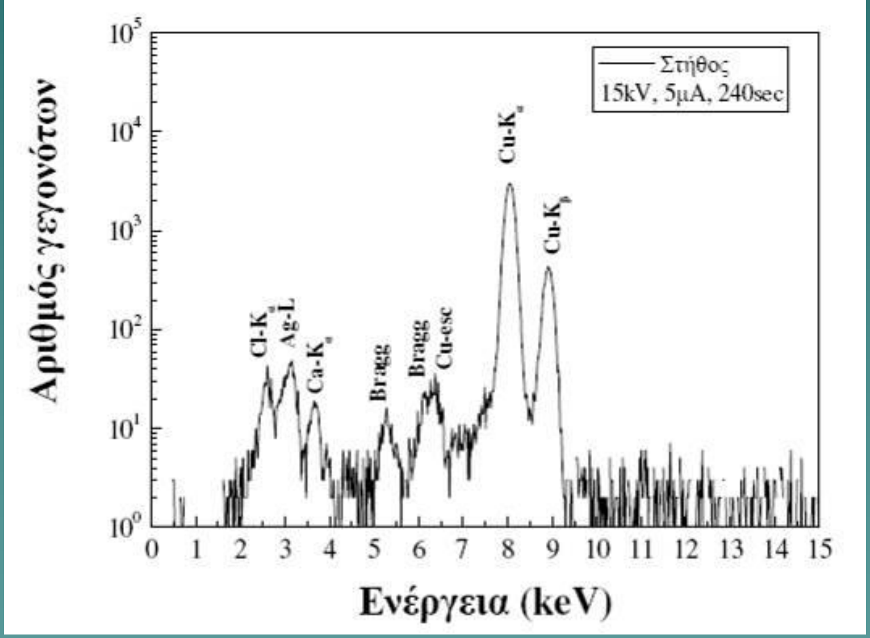




Join in arm

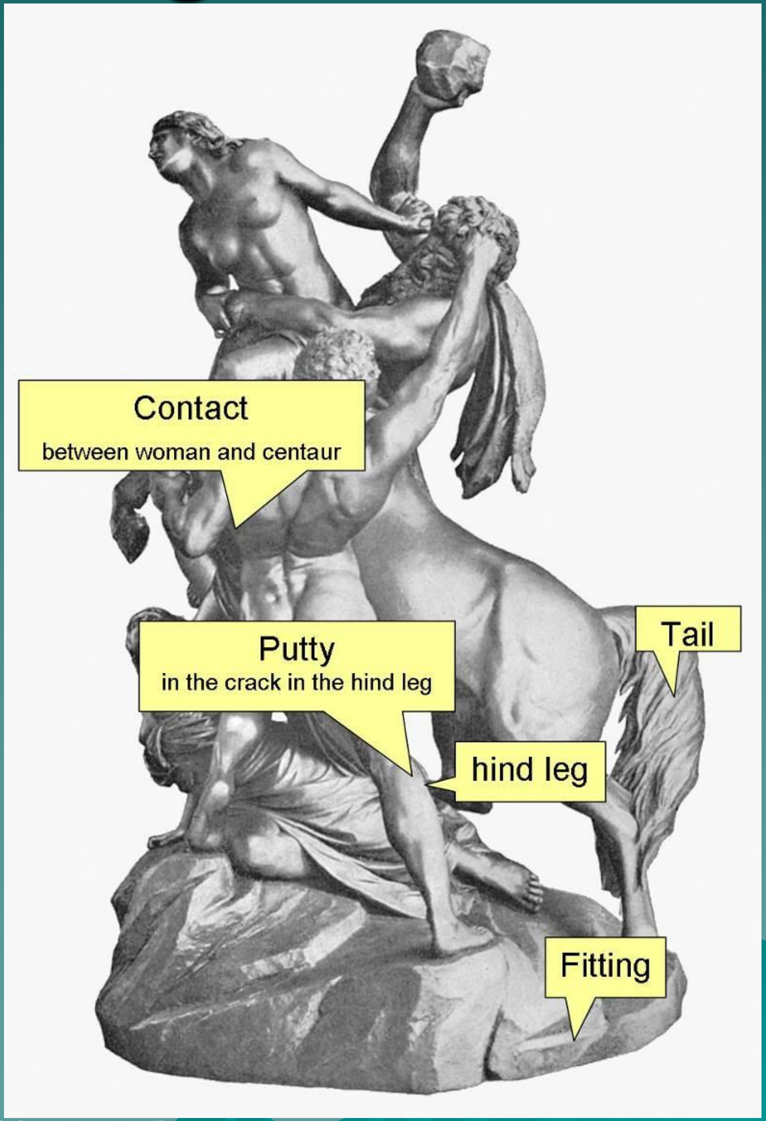
Portable XRF of lying woman chest





Sampling

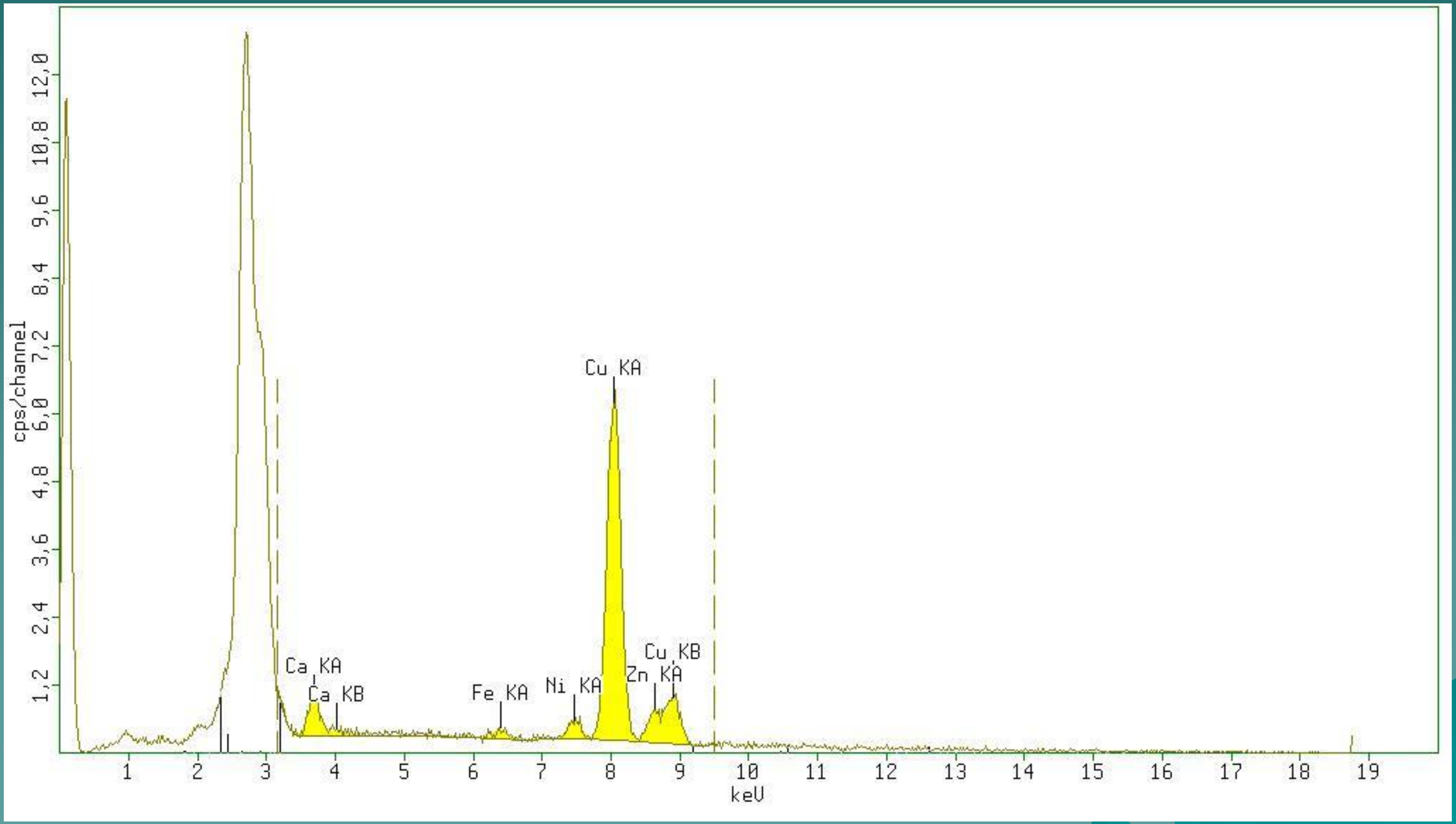
- To get more information about the manufacturing technique it was planned to take some samples for a metallurgical investigation



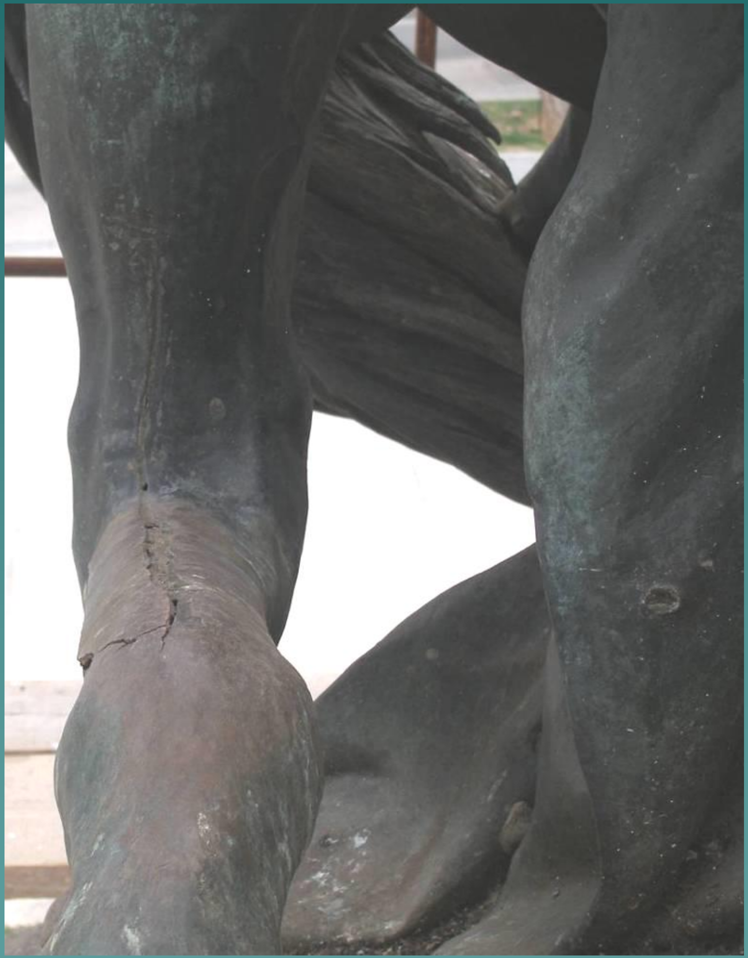
XRF at Bavarian State Monument Laboratory

- Philips MiniPal 4025/00, Rh source, Si detector, Be window, typical acceleration voltage for metallic samples 20-25 kV

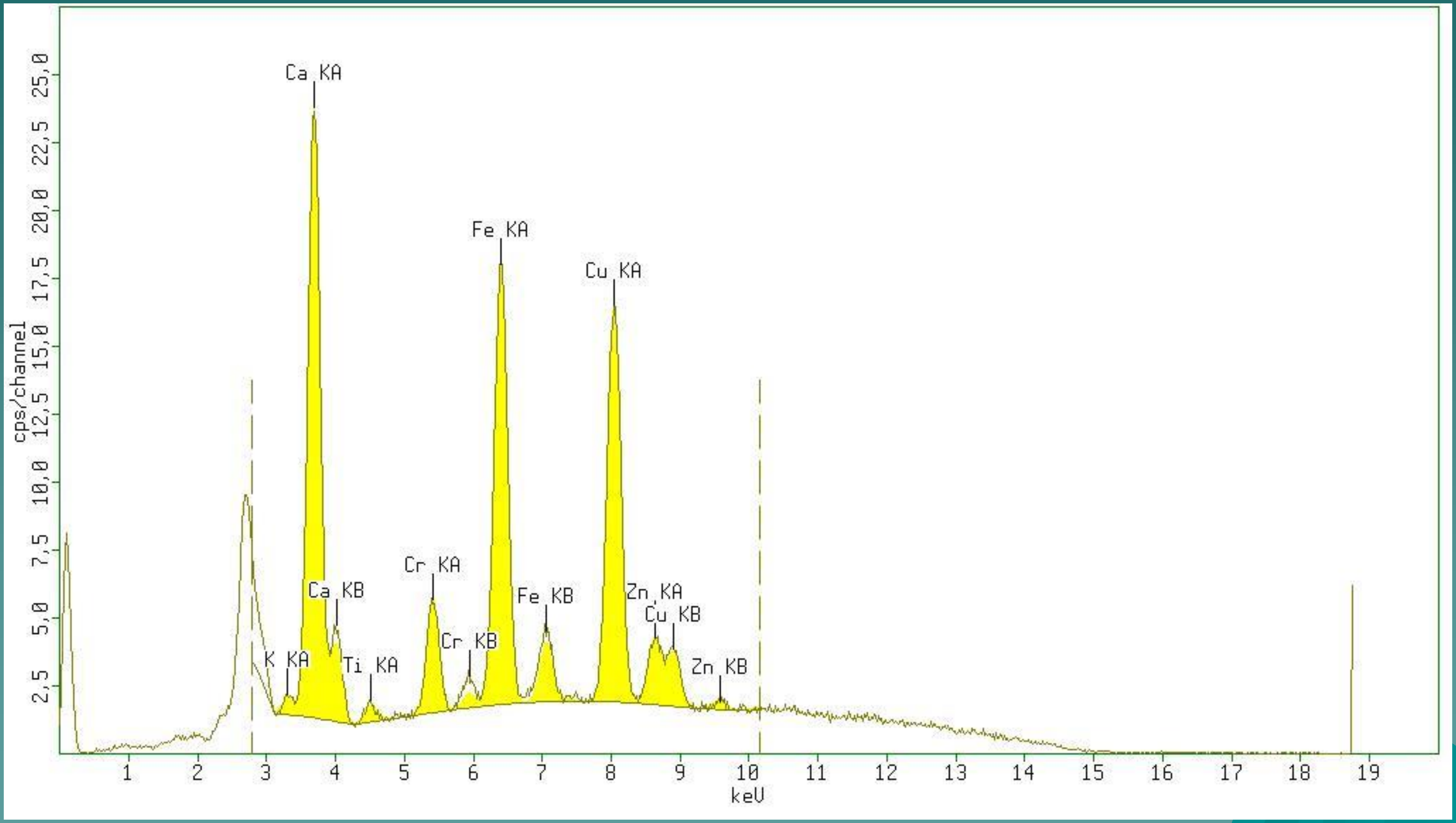
Bar inside Tail contains brass



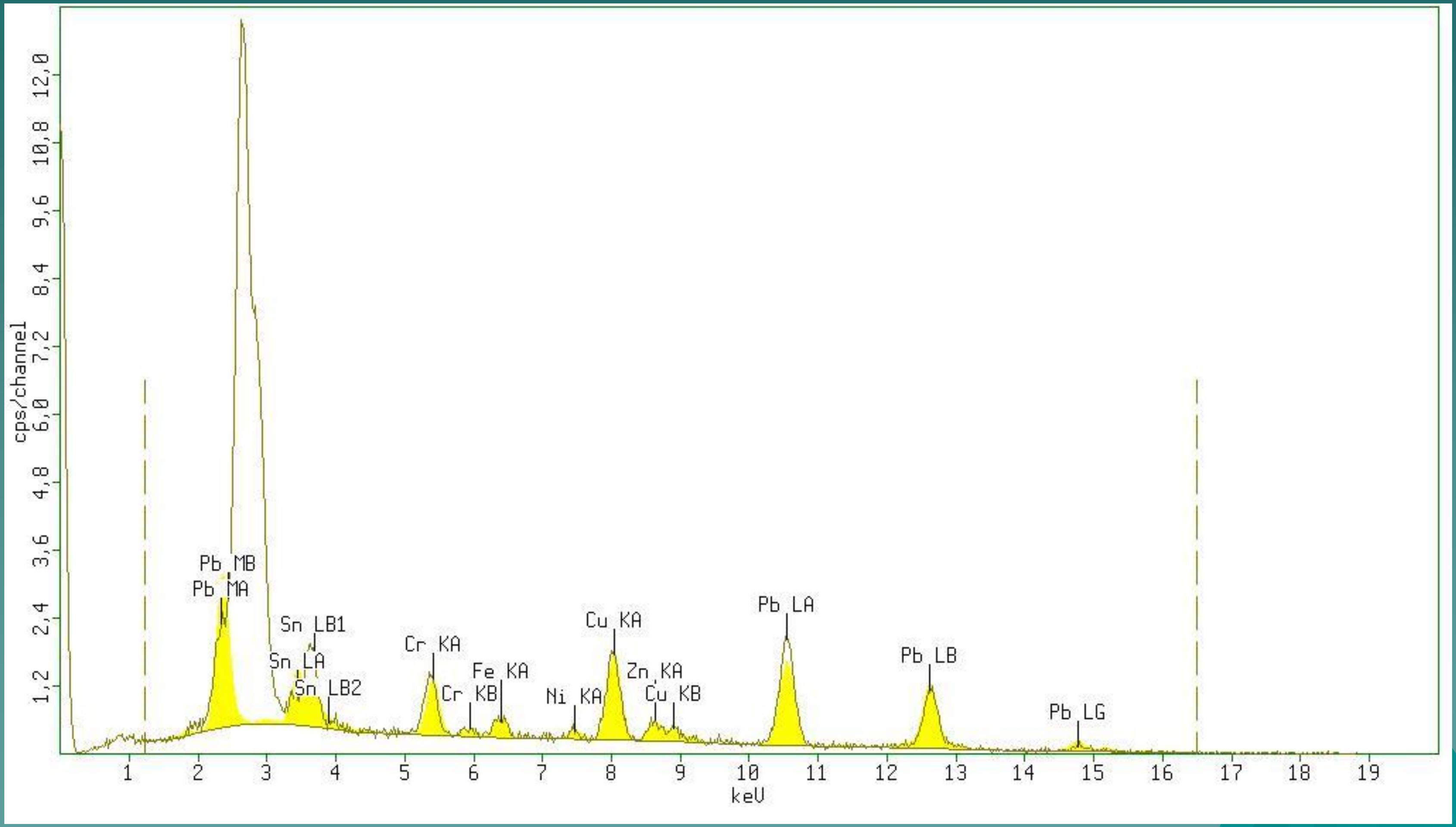
Join and crack: Centaur's right back leg and thigh



Filling material "putty" inside fissure

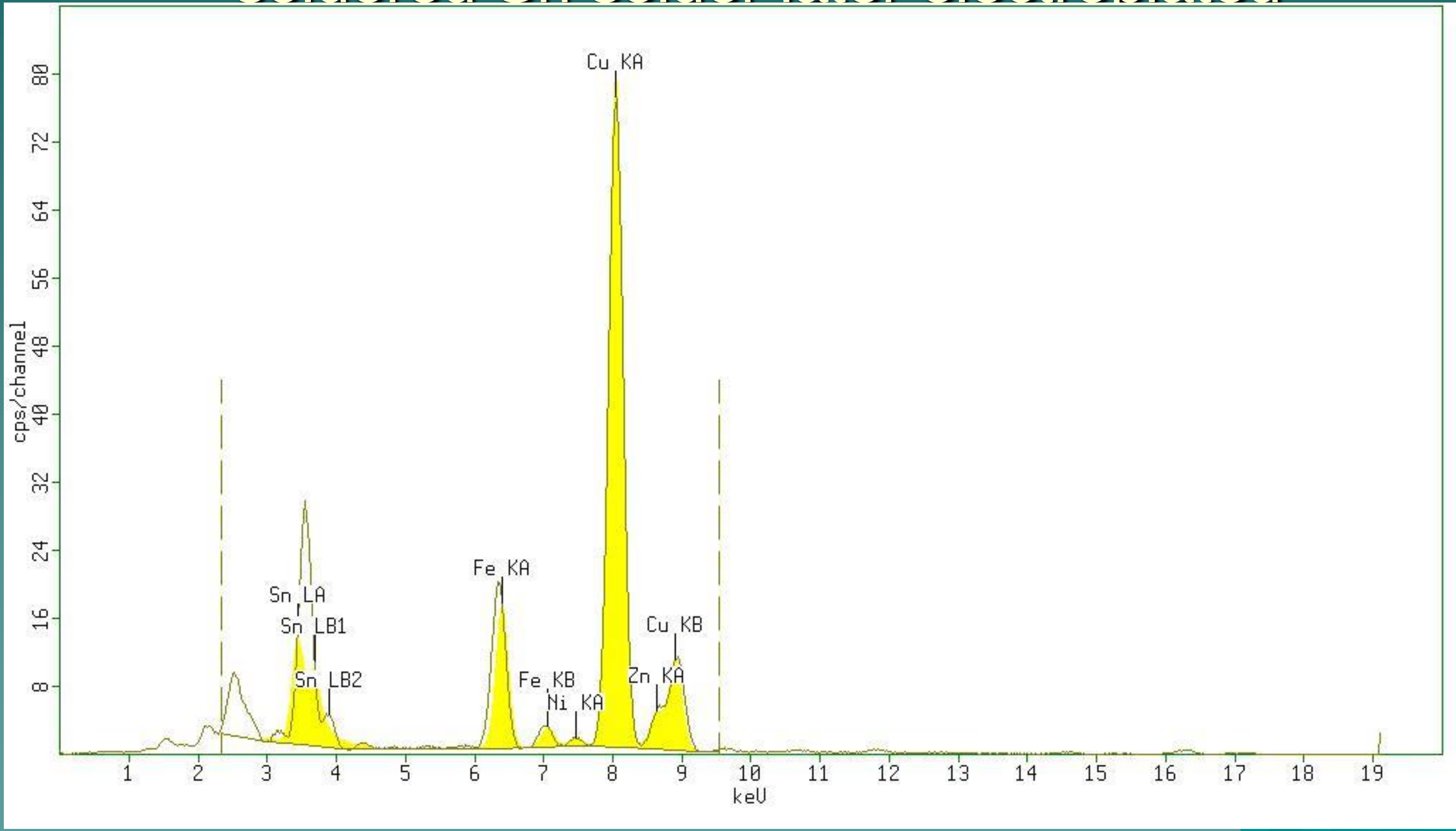


Solder (Contact line) between the lying woman and the centaur.

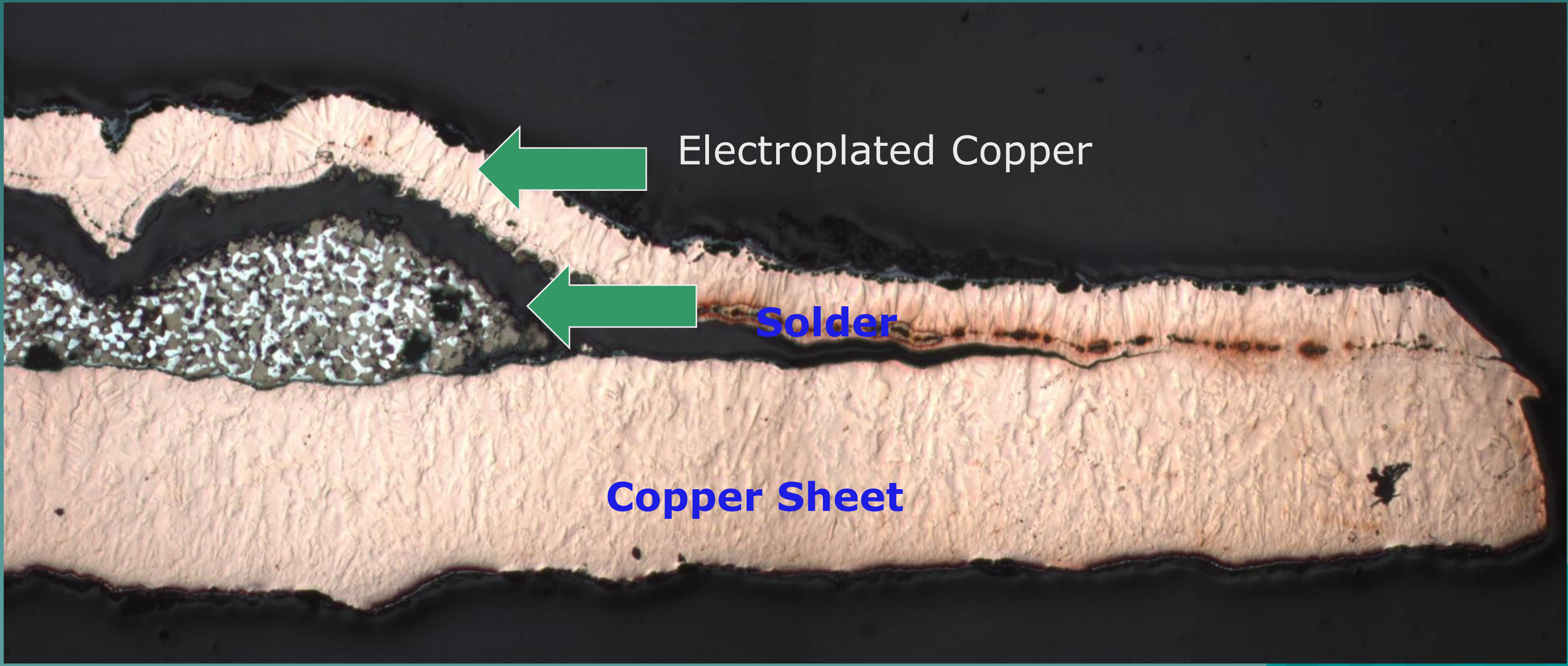


Strap of the Interior Fitting

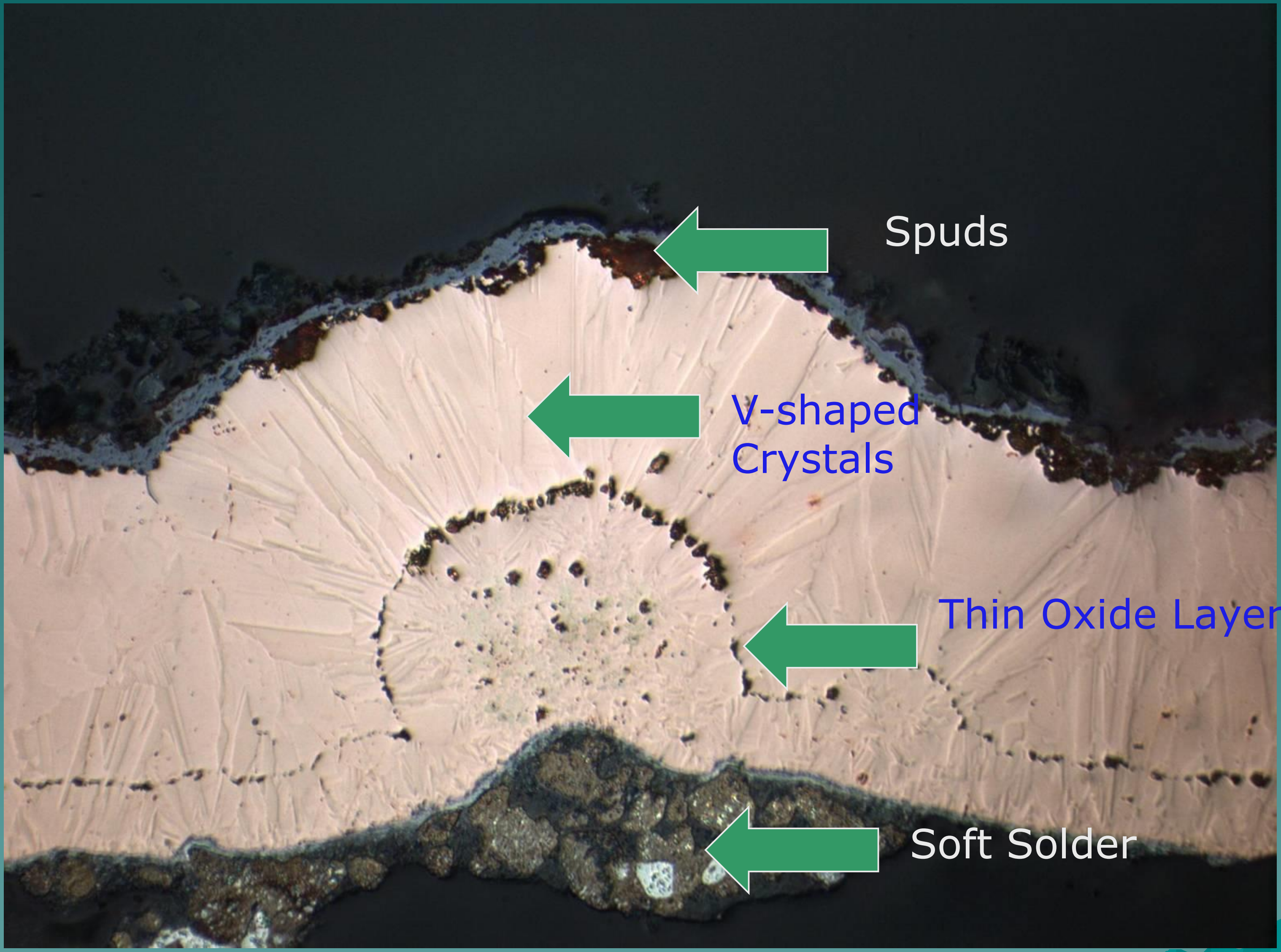
iron stilts inside the plinth fixed by Cu sheet, soldered Sn solder later electroplated



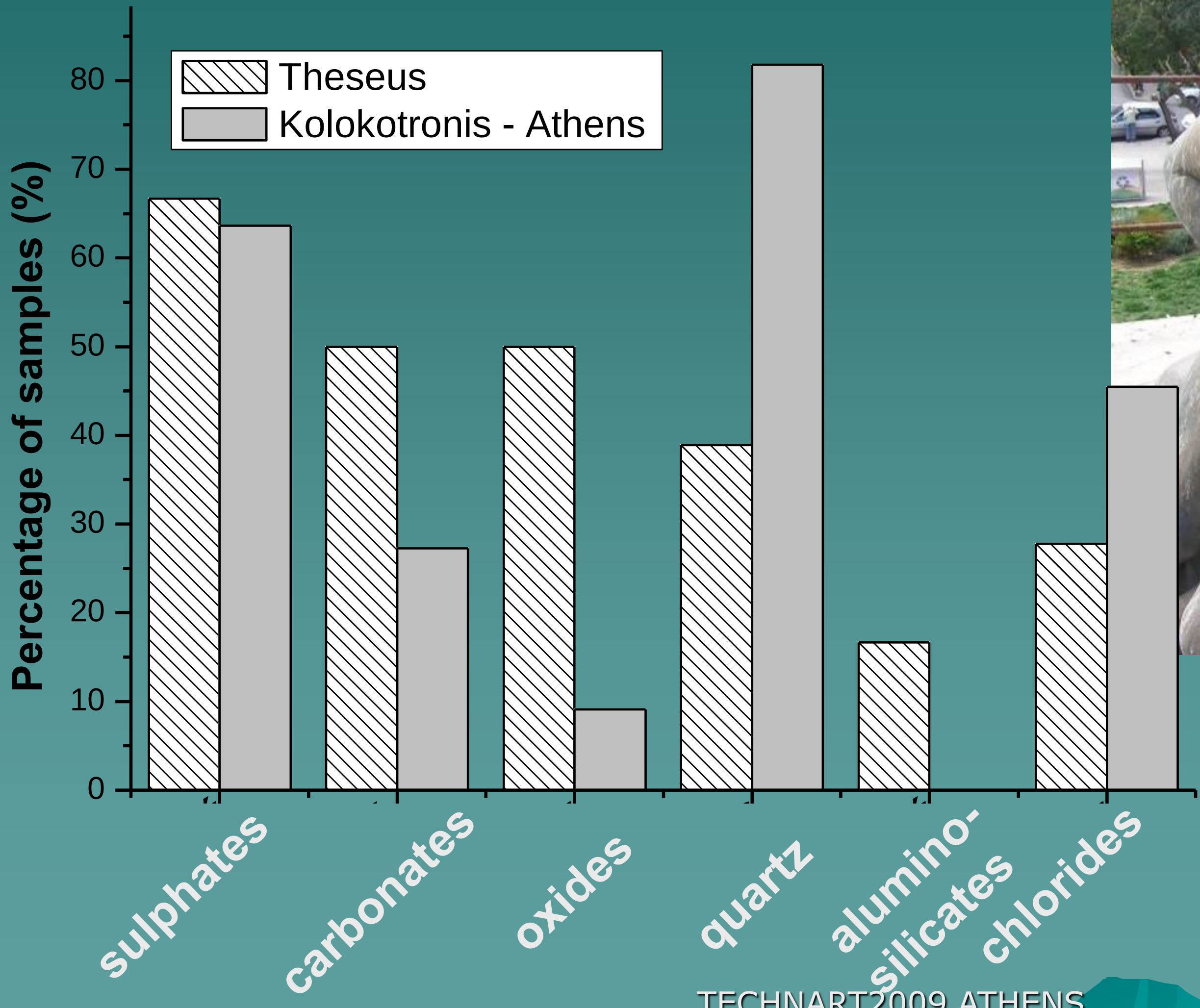
Strap of the interior fitting at plinth stilts inside the plinth were fixed with narrow bands of electroplated copper



Wieland Fischer, Struers GmbH (Photo: M. Mach).


Spuds
V-shaped
Crystals
Thin Oxide Layer
Soft Solder

XRD Analysis



Important Considerations

- Knowledge and experience of person carrying out condition report for the object in question
- Systematic Documentation of every point
- Don't experiment with new materials and tools in the field!
- Team work is key.

In-situ Analysis versus Sampling

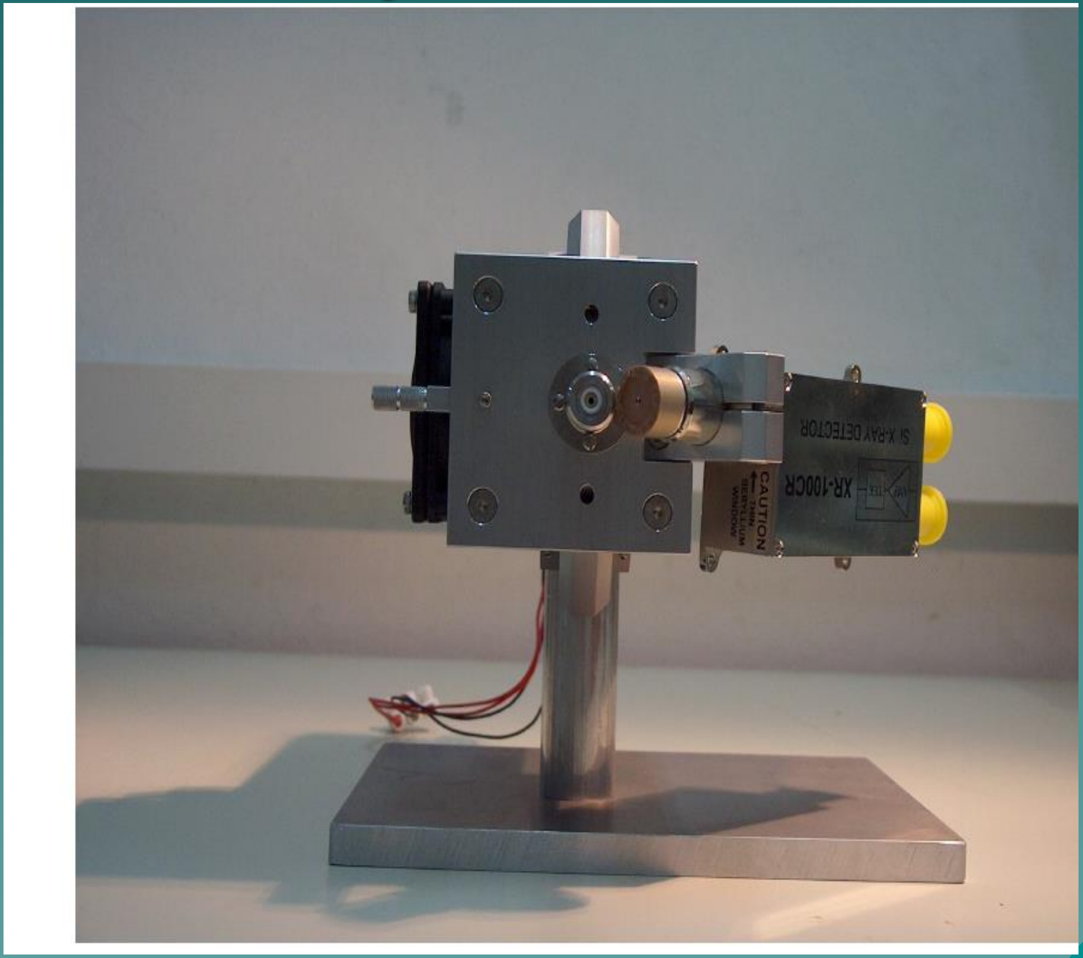
Sampling

- More time for thorough analysis
- Repeat Analysis on similar sample
- Limited as to size and number
- No monitoring

In-situ measurements

- More Measuring points
- Guidance for Sampling Plan
- Monitoring of Treatment
- Variable depending on Conditions

A home built hand-held XRF system




SI X-RAY DETECTOR
XR-100CR

Thanks

Conservators
Maria Giannoulaki
Eleni Kapatou
Thanasis Karabotsos
Maria Mertzani
Maria Petrou
Christos Stefanidis
Dimitris Tsipotas
Amalia Siatou

TEI of Athens
Prof. Nobilakis
Prof. Rokkos
Prof. Labropoulou
Mr. Tzanolinos

Demokritos
Ch. Zarkadas

IGME
Dr. Oikonomou

Municipality of Athens and Nauplion

Eleni Drakaki

Funding by EC program Culture 2000 and Archimedes-Education and Initial Vocational Training Program are gratefully acknowledged